

# PATENT ABSTRACTS OF JAPAN

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## (54) METHOD FOR FORMING SILVER FILM ON COPPER METAL

### (57)Abstract:

**PURPOSE:** To easily form a silver plating on the surface of copper or copper alloy by bringing the above-mentioned surface into contact with an aq. soln. contg. an alkyl imidazole compd., org. acid (salt) and silver nitrate.

**CONSTITUTION:** A treating soln. of pH3.0 to 4.5 formed by adding the alkyl imidazole compd. expressed by formula, the org. acid and the salt of the org. acid to an aq. soln. formed by adding 0.01 to 1.0%, more preferably 0.05 to 0.5% silver nitrate to water is prepd. For example, 2-aminoimidazole is used as the above-mentioned alkyl imidazole compd. and, for example, acetic acid is used as the org. acid, respectively. The org. acid is preferably added in the form of the salt thereof. The above-mentioned treating liquid is usually kept at 20 to 60°C and is brought into contact with the copper or copper alloy for 30 seconds to 5 minutes, by which the silver film is formed on the above-mentioned copper metal. This silver plating is adequate for the surface treatment of terminals, etc., of electronic parts. The silver plating on the small copper metals in the form of grains or powder is possible and the method is suitable for mass production of ornamental materials.



但し、式中Rは長鎖アルキル基、R'は水素原子または低級アルキル基を意味す。

④ 発明の名称 銅系金属に銀被膜を形成する方法

⑤ 特 願 平1-137019

⑥ 出 願 平1(1989)5月29日

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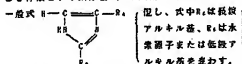
# 明 細 書

## 1. 発明の名称

銅系金属に銀被膜を形成する方法

## 2. 特許請求の範囲

- (1) 下記の一般式で示されるアルキルイミダゾール化合物、有酸素、有機酸の塩及び硝酸銀を含む水増液に、銅あるいは銅合金の表面を浸漬させることを特徴とする銅系金属に銀被膜を形成する方法。



- (2) アルキルイミダゾール化合物として、2-ウンダシルイミダゾールを用いる請求項(1)に記載の銅系金属に銀被膜を形成する方法。
- (3) アルキルイミダゾール化合物として、2-ウンダシル-1-メチルイミダゾールを用いる請求項(1)に記載の銅系金属に銀被膜を形成する方法。

## 3. 発明の詳細な説明

### 産業上の利用分野

この発明は、銅あるいは銅合金の表面に銀被膜

を形成する方法に関するものであり、本発明方法は特にプリント配線基板的銅表面処理に好適である。

### 従来の技術

銀メッキは、通常シアン化アルカリ塩を用いる方法によって行われている。代表的なメッキ浴は、シアン化銀、シアン化カリウム、炭酸カリウム及び光沢剤を所定の割合で水に溶かしたものであり、作業条件としては液温が20〜30℃、電流密度を40〜160A/㎡として行われている。

また還元メッキ法による銀メッキでは、アンモニア性硝酸銀水溶液に対し、還元剤としてロッシェル塩またはホルマリンを用いて行われる。しかしこの方法はメッキ層の膜厚、表面状態等問題があり、工業的には実施されていない。

発明が解決しようとする課題

銀メッキでは毒性の強いシアン化銀、シアン化カリウムを使用するため、環境以上の安全管理が要求される。

また従来方法によれば、電流密度、液温のシッ

ン化カリウム及び硝酸塩の点検など、多くの管理項目及びメッシュ設置が必要である。さらに従来の方法は閉鎖性、閉鎖などの小さい金属の表面にメッシュをすることが出来なかった。

問題を解決するための手段

2位に長鎖アルキル基を有するイミダゾール化合物は、ある種の金属と錯体を形成することが知られている。

例えば、2-ウンデシルイミダゾール及びその誘導体を適当な量の存在下で水に溶解し、この溶液中に腐蝕剤を入れると、アルキルイミダゾールが鋼の表面に析出し化成膜を生成する。(特公開48-17042、特公開49-25621及び特公開49-26183号公報)

本発明者はこのような事実に基づき試験を繰り返した結果、2位に長鎖アルキル基を有するイミダゾール化合物と有機酸を含む水溶液に、銅イオンを添加すると液中でイミダゾール銅錯体を形成し、このイミダゾール銅錯体が鋼表面に析出することを認め、さらに2位に長鎖アルキル基を有す

るイミダゾール化合物と有機酸を含む水溶液中に適当量の硝酸塩を加えた場合、イミダゾール銅錯体が鋼表面に移動し、その酸化還元電位に有機酸塩が存在させて、アルキルイミダゾール有機酸塩の解離を抑制すれば、銅イオンのみが鋼表面に集まり、鋼あるいは銅合金の表面に銅メッキが形成されることを見出し、本発明方法を完成した。

すなわち本発明方法は、鋼あるいは銅合金の表面を2位に長鎖アルキル基を有するイミダゾール化合物と有機酸及び有機酸塩の塩並びに硝酸塩を含む水溶液に接触して、これら金属の表面に金属膜を形成したものである。

本発明の実施に用いるアルキルイミダゾール化合物は、2-アミルイミダゾール、2-ヘプチルイミダゾール、2-デシルイミダゾール、2-ウンデシルイミダゾール、2-ウンデシル-4-メチルイミダゾール、2-ドデシルイミダゾール、2-トリデシルイミダゾール、2-ヘキサデシルイミダゾール、2-ヘプタデシル-4-メチルイミダゾール等であり、これらは水に対して0.01~

5%の範囲、好ましくは0.5~2%の割合で添加する。

本発明方法の実施においては、前記アルキルイミダゾール化合物の水に対する溶解性を高めるために、有機酸を加えて水に可溶性の塩とすべきである。

本発明の実施に適する有機酸は、酢酸、カプリン酸、グリコール酸、パラエトロ安息香酸、パラトルエンスルホン酸、ピクリン酸、樟酸、琥珀酸、マレイン酸、アマル酸、酒石酸、アジピン酸等であり、これら有機酸は水に対して0.01~10%の範囲、好ましくは0.05~2%の割合で添加する。

本発明方法の実施に当たっては、処理水溶液中に有機酸塩が存在するように有機酸塩を添加するかあるいは有機酸を含む処理液に塩基性物質を加えて、アルキルイミダゾール有機酸塩の解離を抑制すべきである。

本発明の実施において、腐蝕性有機酸の塩を形成するために使用する塩基性物質は、アルカリ金属

あるいはアルカリ土類金属の水酸化物または炭酸塩、アンモニウムまたはアンモニウム塩、メチルアミン、エチルアミン、エタノールアミン等のアミン類が好適である。

また本発明における硝酸塩の添加量は、水に対して0.01~1.0%、好ましくは0.05~0.5%の割合で添加し、これらアルキルイミダゾール化合物、有機酸、有機酸の塩及び硝酸塩を含む処理液のpHは、3.0~4.5の範囲に維持することが望ましい。

本発明方法の実施において、前記処理液を通常20~60度の温度範囲に保ち、鋼あるいは銅合金を30秒~5分間浸漬すれば良い。

作 用

2位に長鎖アルキル基を有するイミダゾール化合物は、適当な硝酸塩で鋼の表面に移行し析出する。アルキルイミダゾールは常温では水に溶けにくい有機酸水溶液にはよく溶ける。有機酸水溶液中でイオン化したイミダゾールは銅と強い化学反応性を示し、銅と錯体を形成し、鋼の表面に銅分子の

膜を形成する。

このようにしてできた単分子の膜の上に長鎖アルキル基のファンデルワースの結合力によってアルキルイミダゾールの膜が次々と重なり合って膜が成長し、またイミダゾール同士の水素結合力によってよりしっかりと膜になる。

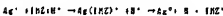
このアルキルイミダゾール化合物と有機酸を含む水溶液のなかで、金属イオンが含まれた場合、 $\text{pH } 3.0 \sim 4.5$  の領域で金属イオンはイミダゾールと水溶性の錯体を形成する。これらの錯体はイミダゾールの付着力に影響を及ぼす。しかし $\text{pH}$ が所定の値より高くなると、イミダゾールと金属が不溶性の錯体を作って沈降する。

2位に長鎖アルキル基を有するイミダゾール化合物と有機酸を含む水溶液に硝酸銀を加えると、 $\text{pH } 4.0$  以下の領域で処理水溶液は安定だが、それ以上の $\text{pH}$ になれば銀とイミダゾールの不溶性の錯体を生じて白濁する。 $\text{pH } 3.0 \sim 4.0$  の間で処理された銅表面は、一部金属膜光沢があるもののイミダゾール及び低い金属銀の入り混った膜ができ、

塩酸水溶液を用いてイミダゾール化合物を除去しても、金属銀の表面は磨られない。これらの表面状態は有機酸の量を加え $\text{pH}$ を調整し昇させ、吸着剤としてイミダゾールの解離を抑制することによって改善される。

有機酸の量を添加することにより、 $\text{pH}$ は上昇するがイミダゾールの飽和度は低下する。有機酸の量を添加することによって金属光沢をした銀の膜が下に、その上にイミダゾールの被膜が形成されるようになる。両金属からこのように二層に別れた膜形成に変化する理由は、まず銀の単分子膜が銀の表面に形成されるためと思われる。銀の単分子膜が最初は何の表面にできるかは、銀イオンがイミダゾール銀錯体の形で、アルキルイミダゾールの膜形成能力により銅表面まで運ばれ、銀イオンのみ銅表面に移行するためと考えられる。これは恐らくある $\text{pH}$ 領域を保持した膜形成で、錯体中の銀が錯体中からイオン化傾向の高い銅に移行するためである。銀イオンのみが銅表面に移行せず、イミダゾール銀錯体の形で表面に附

着すると複合膜となる。銀イオンが錯体の形で銅表面に移動し還元されて銀メッキが形成され、銀イオンが単体で銅の表面でイオン化傾向の違いにより還元されて析出すると密着性の悪い脆い被膜となる。銀と可溶性の錯体をつけたアルキルイミダゾール(1Mと略称する)は、金属表面で膜を還元しているものと区別される。



以下実施例及び参考例により本発明方法をさらに具体的に説明する。

#### 実施例1

2-ウンデシル-4-メチルイミダゾール1.0gに酢酸5.0mlを加えて2-ウンデシル-4-メチルイミダゾールを溶解し、さらに純水100mlを加えてよく攪拌し、毎一水溶液とし、この水溶液に硝酸銀0.1g、硝酸アンモニウム1.0gを加えてよく攪拌して $\text{pH } 4.04$ の処理液を調整した。他方 $4\text{cm} \times 4\text{cm}$ の銅箔張板の銅表面をスコッチブライトで細粒研磨し、これを0.5%塩酸水溶液に30秒浸漬のち純水で水洗し、この銅箔張板を35℃の蒸

気中に維持された飽和処理液に3分間浸漬し、取り出した銅箔張板を0.5%塩酸水溶液に20秒浸漬し、水洗乾燥すると、銅箔張板の銅面に均一な銀のメッキ層が形成された。

#### 参考例1

2-ウンデシル-4-メチルイミダゾール1.0gに酢酸5.0mlを加え、2-ウンデシル-4-メチルイミダゾールを溶解させたのち、これに純水100ml及び硝酸銀0.1gを加えて、 $\text{pH } 3.15$ の処理液を調整し、実施例1と同様の表面処理をした銅箔張板を飽和処理液に35℃の温度で3分間浸漬したところ、合成樹脂の銅面には銅と置換された層の膜。銀光沢を呈す銀及びイミダゾールの入り混った複合膜が形成され、これを0.5%塩酸水溶液に浸漬しても銀光沢の表面が磨られなかった。

#### 参考例2

実施例1において、2-ウンデシル-4-メチルイミダゾールの代わりに、2-メチルイミダゾールを用いた以外は、全く同じ処理条件で銅箔張板の銅表面に対する銀メッキ処理を試みたが、

刷の表面には、銅と覆膜された密着性の悪い藍色の膜のみが析出し、銀光沢の表面を形成することができなかった。

## 実施例2

実施例1において、2-ウンデシル-4-メチルイミダゾールの代わりに、2-ウンデシルイミダゾールを用いた以外は、全く同じ処理条件で銅箔積層板の銅表面に対する銀メッキ処理を行ったところ、銅箔積層板の銅面は、実施例1と同様の銀メッキが形成された。

## 実施例3

実施例1において、酢酸アンモニウム1.0gの代わりに、クエン酸アンモニウム1.0gを添加したpH3.00の処理液を用いた以外は、全く同じ処理条件として銅箔積層板の銅面に銀メッキ処理を行った結果、銅箔積層板の銅面に銀光沢の表面が形成された。

## 実施例4

実施例1において、酢酸の代わりに酢酸、酢酸アンモニウムの代わりに酢酸アンモニウムを銅箔

したpH4.00の処理液を用いた以外は、全く同じ処理条件によって銅箔積層板の銅面に銀メッキ処理を行ったところ、銅箔積層板の銅面には均一な銀メッキを生成した。

## 実施例5

銅粉を5%高純度アンモニウム水溶液に10時間攪拌浸漬したのち、蒸留し水洗して、表面が清浄化された銅粉を調整し、これを実施例1において調整した処理液に攪拌下で1分間接触させたのち、銅粉を濾別し、0.5%塩酸水溶液で洗浄し水洗乾燥して、表面に銅が被覆した銅粉を得た。

## 発明の効果

本発明方法は、銅あるいは銅合金の表面に銀メッキを簡単に施すことができるので、電気部品における端子等の表面処理に好適であり、また粒状あるいは粉末状の小さい銅合金に対する銀メッキが可能となり、塗料材料の量産に適するなど実産業の効果は多大である。

特許出願人 西田化成工業株式会社



特 許 申 請 書

平成1年1月13日

特許庁長官 殿

## 1. 事件の表示

平成1年特許願第137019号

## 2. 発明の名称

銅系金属に銀被膜を形成する方法

## 3. 補正をする者

事件との関係：特許出願人

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(〒753 84 0377-22-4111)

## 4. 発明の要旨

自 発

## 5. 補正の趣意

明細書の特許請求の範囲の欄

## 6. 補正の趣意

特許請求の範囲を別紙のとおり補正する。

方式  
審査

以 上

## 補正後の特許請求の範囲

(1) 下記的一般式で示されるアルキルイミダゾール化合物、有機酸、有機酸の塩及び硝酸銀を含む水溶液に、銅あるいは銅合金の表面に銀被膜を形成することを特徴とする銅系金属に銀被膜を形成する方法。

一般式  $\text{H}-\text{C}=\text{C}-\text{R}_2$  (但し、式中 $\text{R}_2$ は長鎖アルキル基、 $\text{R}_1$ は水素原子または低級アルキル基を表す。

(2) アルキルイミダゾール化合物として、2-ウンデシルイミダゾールを用いる請求項(1)に記載の銅系金属に銀被膜を形成する方法。

(3) アルキルイミダゾール化合物として、2-ウンデシル-4-メチルイミダゾールを用いる請求項(1)に記載の銅系金属に銀被膜を形成する方法。

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(54) Title of the invention	METHOD FOR FORMING SILVER FILM ON COPPER-BASED METAL
(21) Japanese Patent Application	H01-137019
(22) Date of Application	May 29, 1989
(72) Inventor	Shūji Yoshida
(71) Applicant	Shikoku Chemical Corp.
	2-2-20-401 Nishimoto-chō, Marugame-shi, Kagawa-ken
	147-1 Minato-chō, Marugame-shi, Kagawa-ken

## SPECIFICATION

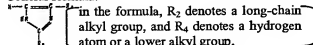
## 1. TITLE OF THE INVENTION

Method for Forming Silver Film on Copper-Based Metal

## 2. SCOPE OF PATENT CLAIMS

1. A method for forming a silver film on copper-based metal, characterized in that the surface of copper or copper alloy is brought into contact with an aqueous solution that contains an alkyl imidazole compound represented by the general formula presented below:

General formula:



in the formula, R<sub>2</sub> denotes a long-chain alkyl group, and R<sub>4</sub> denotes a hydrogen atom or a lower alkyl group,

an organic acid, an organic acid salt, and silver nitrate.

(2) The method for forming a silver film on copper-based metal according to claim 1, wherein 2-undecylimidazole is used as the alkyl imidazole compound.

(4) The method for forming a silver film on copper-based metal according to claim 1, wherein 2-methylimidazole is used as the alkyl imidazole compound.

## 3. DETAILED DESCRIPTION OF THE INVENTION

## FIELD OF INDUSTRIAL UTILIZATION

The present invention relates to a method for forming a silver film on the surface of copper or a copper alloy. The method of the present invention is particularly desirable for copper surface processing of printed wiring substrates.

## PRIOR ART

Silver plating has been carried out by methods that employ common alkali cyanine baths. Typical plating baths are produced by dissolving silver cyanide, potassium cyanide, potassium carbonate, and a brightener at predetermined ratios in water. The solution temperature under operating conditions is 20 to 30°C, and the operation is carried out at a current density of 40 to 160 A/m<sup>2</sup>.

With silver plating carried out by reduction plating, Rochelle salt or formalin is dissolved as reducing agent in ammoniacal silver nitrate aqueous solution.

However, there have been problems with film thickness and surface condition of the plated layer with this method, and such methods have not been industrially implemented.

## PROBLEMS TO BE SOLVED BY THE INVENTION

With silver plating, highly toxic silver cyanide and potassium cyanide are used, and so safety controls are required when handling.

With conventional methods, numerous controls are required, such as monitoring of current density as well as silver and free potassium cyanide concentrations, and a large amount of plating equipment is also required. In addition, plating on small metal surfaces such as copper particles and copper powder has not been possible with conventional methods.

#### MEANS FOR SOLVING THE PROBLEMS

It is known that imidazole compounds having long-chain alkyl groups in the 2-position form complexes with some types of metals.

For example, when 2-undecylimidazole and derivatives thereof are dissolved in water in the presence of a suitable acid, and a copper plate is introduced into this solution, the alkyl imidazole precipitates on the surface of the copper, forming a chemical conversion film (Japanese Examined Patent Application Nos. 46-17042, 48-25621, and 49-26183).

The inventors of the present invention, as a result of repeated experimentation based on these facts, arrived at the present invention upon discovering that: if an imidazole compound having long-chain alkyl groups in the 2-position is dissolved in aqueous solution containing organic acid, and copper ions are added, then imidazole-copper complex is formed and the imidazole complex is deposited on the copper surface; if silver nitrate is added in a suitable amount to an aqueous solution containing organic acid and an imidazole compound having long-chain alkyl groups in the 2-position, then imidazole complex is transferred to the copper surface; and if organic acid salt is included in the treated aqueous solution at this time, only silver ions will collect at the copper surface if dissociation of the alkyl imidazole organic acid salt is inhibited, and silver plating will be formed on the surface of the copper or copper alloy.

Specifically, the method of the present invention involves forming a metallic silver film on the surfaces of these metals by bringing the surface of copper or copper alloy into contact with an aqueous solution containing imidazole having long-chain alkyl groups at the 2-position, organic acid, organic acid salt, and silver nitrate.

Examples of alkyl imidazole compounds that are suitable for implementation of the present invention include 2-amylimidazole, 2-heptylimidazole, 2-decylimidazole, 2-undecylimidazole, 2-undecyl-4-methylimidazole, 2-dodecylimidazole, 2-tridecylimidazole, 2-heptadecylimidazole, and 2-

heptadecyl-4-methylimidazole.

These compounds are added at ratios in the range of 0.01 to 5%, preferably 0.5 to 2%.

In implementing the method of the present invention, the organic acid should be added in the form of a salt that is soluble in water in order to increase the solubility of the alkyl imidazole compound in water.

Organic acids that are suitable for implementing the present invention include acetic acid, capric acid, glycolic acid, paranitrobenzoic acid, paratoluenesulfonic acid, picric acid, oxalic acid, sulfuric acid, maleic acid, fumaric acid, tartaric acid, and adipic acid. These organic acids are added at ratios in the range of 0.01 to 10%, preferably 0.05 to 2%, with respect to water.

In working the method of the present invention, organic acid salt is added, or a basic substance is added to treatment solution containing organic acid so that organic acid salt will be present in the aqueous treatment solution, thereby inhibiting dissociation of the alkyl imidazole organic acid salt.

In implementing the present invention, basic substances that are used in order to form organic acid salts include alkaline metal or alkaline earth metal hydroxides or carboxylates, ammonia or ammonium salts, methylamine, ethylamine, ethanolamine, and other amines.

In addition, the ratio of the added amount of silver nitrate in the present invention is 0.01 to 1.0%, preferably 0.05 to 0.5%, with respect to water. The pH of the treatment solution containing the alkyl imidazole compound, the organic acid, organic acid salt, and the silver nitrate is preferably in the range of 3.0 to 4.5.

In working the method of the present invention, it is normally preferable for the treatment solution to be maintained at a temperature in the range of 20 to 60°C and for the copper or copper alloy to be in contact for from 30 seconds to 5 minutes.

#### OPERATION

The imidazole compound having long-chain alkyl groups in the 2-position is transferred to the surface of the copper and is deposited thereupon in suitable pH ranges. Alkyl imidazoles are normally insoluble in water but dissolve readily in acidic aqueous solutions. Imidazole that has been ionized in acidic aqueous solution exhibits strong chemical reactivity with respect to copper, forming complexes with the copper. A film of individual molecules is thus formed on the surface of the copper.

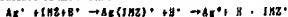
The alkyl imidazole progressively accumulates due to the van der Waals bonding strength of the long-chain alkyl groups in the film of individual molecules that has been produced in this manner, and the film thus grows. In addition, a solid film is formed due to hydrogen bonding forces between the imidazoles.

When metal ions are included in the aqueous solution containing organic acid and alkyl imidazole compound, the metal ions will form water-soluble complexes with the imidazole in a pH range of 3.0 to 4.5. These complexes influence the adhesion force of the imidazole. However, if the pH is greater than a specific value, the imidazole and metal will form insoluble complexes that will sediment.

When silver nitrate is added to the aqueous solution containing the imidazole compound having 2-position long-chain alkyl groups and organic acid, the aqueous treatment solution will be stable in the pH range of 4.0 or less. Insoluble complexes between imidazole and silver will be formed at higher pH values, and clouding will occur. With copper surfaces that are treated at pH values of from 3.0 to 4.0, mixed films containing black metallic silver and imidazole having partial metallic silver luster are obtained, but a metallic silver surface will not be obtained, even if the imidazole compound is removed using hydrochloric acid aqueous solution. The condition of the surface is improved if the pH is increased slightly by adding organic acid salt, thereby suppressing imidazole decomposition by producing a buffered system.

The pH is increased by adding organic acid salt, but the film thickness of the imidazole will decrease. In addition, a silver film having metallic luster will be produced as a lower layer if an organic acid salt is added, and an imidazole film will be formed thereupon. The reason that a film that is separated into two distinct layers is formed by the complex film in this manner is that a monomolecular film of silver molecules is first formed on the surface of the copper. Initial formation of the film of individual silver molecules on the surface of copper is thought to occur because, in the form of the imidazole complex, the silver ions will move to the surface of the copper due to the film formation capacity of the alkyl imidazole, and only silver ions will migrate to the surface of the copper. In buffered systems that are maintained at a given pH range, this is likely because the silver in the complex migrates from the complex to the copper which has a high ionization tendency. Silver ions alone cannot migrate to the surface of the copper, and deposition onto the surface occurs in the form of imidazole silver complex, thereby producing a composite film. Silver plating is formed when the silver ions migrate to the surface of the copper in the

form of a complex and then undergo reduction. The silver ions are individually substituted at the surface of the copper due to the difference in ionization tendency, thereby being deposited as a black film with poor density. It is conjectured that the alkyl imidazole ("IMZ" below) that has produced the soluble complex with silver reduces the silver at the surface of the metal.



The method of the present invention is described in additional detail below by providing examples of embodiment and reference examples.

#### Example of Embodiment 1

5.0 mL of acetic acid was added to 1.0 g of 2-undecyl-4-methylimidazole, thereby dissolving the 2-undecyl-4-methylimidazole. 100 mL of purified water was then added, and the solution was stirred well to produce a uniform aqueous solution. 0.1 g of silver nitrate and 1.0 g of ammonium acetate were added to this aqueous solution, and the solution was stirred well to prepare an aqueous solution with a pH of 4.04. The surface of a 4 × 4 cm square copper-clad laminated plate was wet-polished with Scotch-Brite after immersion for 30 sec in a 0.5% hydrochloric acid aqueous solution and washed with purified water. The copper-clad laminated plate was then immersed for 3 min in the aforementioned treatment solution while maintaining a temperature of 35°C. The copper-clad laminated plate that was removed was then immersed for 20 sec in a 0.5% hydrochloric acid aqueous solution, rinsed with water, and dried to obtain a uniform silver plated layer on the copper-clad laminated plate.

#### Reference Example 1

5.0 mL of acetic acid was added to 1.0 g of 2-undecyl-4-methylimidazole, and the 2-undecyl-4-methylimidazole was dissolved. 100 mL of purified water and 0.1 g of silver nitrate were then added to prepare a treatment solution with a pH of 3.15. A copper-clad laminated plate that had been subjected to the same surface treatment as in Example of Embodiment 1 was then immersed for 3 min in the aforementioned treatment solution at a temperature of 35°C. At the copper surface of the synthetic resin, a composite film was thus formed that contained a mixture of black silver that was substituted for the copper, silver that exhibited silver luster, and imidazole. A surface having silver luster was not obtained, even when immersed in 0.5% hydrochloric acid aqueous solution.

#### Reference Example 2

With the exception that 2-methylimidazole was used instead of 2-undecyl-4-methylimidazole in Example of Embodiment 1, a silver plating treatment was attempted on the copper surface of a copper-clad laminated plate under exactly the same treatment



conditions. However, only black silver with poor density resulting from copper substitution was deposited on the surface of the copper, and a surface having silver luster could not be formed.

#### Example of Embodiment 2

With the exception that 2-undecylimidazole was used instead of 2-undecyl-4-methylimidazole in Example of Embodiment 1, a silver plating treatment was carried out on the copper surface of a copper-clad laminated plate under exactly the same conditions. Silver plating similar to that of Example of Embodiment 1 was formed on the copper surface of the copper-clad laminated plate.

#### Example of Embodiment 3

With the exception that a treatment solution with a pH of 3.80 was produced by adding 1.0 g of ammonium citrate instead of 1.0 g of ammonium acetate in Example of Embodiment 1, a silver plating treatment was carried out on the copper surface of a copper-clad laminated plate under exactly the same conditions. A surface with silver luster was formed on the copper surface of the copper-clad laminated plate.

#### Example of Embodiment 4

With the exception that a treatment solution with a pH of 4.00 was produced by using formic acid instead of acetic acid and by using ammonium formate instead of ammonium acetate in Example of Embodiment 1, a silver plating treatment was carried out on the copper surface of a copper-clad laminated plate under exactly the same conditions. A uniform silver plating layer was obtained on the copper surface of the copper-clad laminated plate.

#### Example of Embodiment 5

Copper powder was immersed for 10 sec in a 5% ammonium persulfate aqueous solution, the solution was passed through a filter, and the material was washed with water. Copper powder having a clean surface was thus prepared. This material was then brought into contact with the treatment solution prepared in Example of Embodiment 1 for 1 min while stirring. The copper powder was then filtered, washed with a 0.5% hydrochloric acid aqueous solution, rinsed with water, and dried to obtain copper powder having silver affixed to its surface.

#### EFFECT OF THE INVENTION

The method of the present invention allows silver plating to be easily formed on the surface of copper or copper alloy and is thus suitable for the surface treatments of terminals or the like in electrical components. In addition, silver plating can be performed on small-size copper metal materials such as particles or powder, and considerable practical effects are thus achieved in regard to the mass production of decorative materials.

Patent Applicant: Shikoku Chemical Corp.

[seal: illegible]

Procedural Corrections

July 13, 1989

Patent Office Commissioner:

#### 1. Indication of the Case:

Heisei 1 [1989], Patent Application No. 137019

#### 2. Title of the invention:

Method for Forming a Silver Film on Copper-Based Metal

#### 3. Person making corrections:

Relationship to Case: Patent Applicant  
147-1 Minato-chō, Marugame-shi, Kagawa-ken  
Shikoku Chemical Corporation  
Representative: Arashi Akazawa [seal: illegible]  
(Postal code: 763 Tel: 0877-22-4111)

#### 4. Date Correction Ordered:

Voluntary

#### 5. Subject of correction:

Claims section of the Specification.

#### 6. Content of correction:

The claims are to be corrected as indicated below.

Formal

Inspection [seal: illegible]

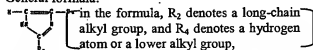
[stamp: Patent Office / July 15, 1989 / [illegible]]

End

Corrected scope of patent claims:

(1) A method for forming a silver film on copper-based metal, characterized in that the surface of copper or copper alloy is brought into contact with an aqueous solution that contains an alkyl imidazole compound represented by the general formula presented below:

General formula:



an organic acid, an organic acid salt, and silver nitrate.

(2) The method for forming a silver film on copper-based metal according to claim (1), wherein 2-undecylimidazole is used as the alkyl imidazole compound.

(3) The method for forming a silver film on copper-based metal according to claim (1), wherein 2-undecyl-4-methylimidazole is used as the alkyl imidazole compound.



# TRANSPERFECT

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I, Charlene Murray, hereby certify that the following is, to the best of my knowledge and belief, a true and accurate translation of the following document, "Japanese Unexamined Patent Application Publication No. H03-2379", from Japanese into English.

Charlene Murray

Sworn to before me this

Wednesday, May 04, 2011

Signature, Notary Public

Stephanie Dill  
Notary Public, State of New York  
No. 01D18180934  
Qualified in NEW YORK County  
Commission Expires Jan 22, 2012

Stamp, Notary Public